

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C11D 3/386	A1	(11) International Publication Number: WO 00/63335 (43) International Publication Date: 26 October 2000 (26.10.00)
(21) International Application Number: PCT/US00/10388 (22) International Filing Date: 18 April 2000 (18.04.00) (30) Priority Data: 60/130,041 19 April 1999 (19.04.99) US (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): SONG, Xiaoqing [CN/US]; 6594 Tylers Crossing, West Chester, OH 45069 (US). FOLEY, Peter, Robert [GB/US]; 621 E. Mehring Way, Apt. 906, Cincinnati, OH 45202 (US). LEYEN-DECKER, Mary, Ruth [US/US]; 3481 Ebenezer Road, Cincinnati, OH 45248 (US). SADLOWSKI, Eugene, Steven [US/US]; 9980 Pebbleknoll Drive, Cincinnati, OH 45252 (US). PIERONI, Lucio [IT/US]; 2219 Eastern Avenue, Cincinnati, OH 45202 (US). PAINTER, Jeffrey, Donald [US/US]; 11662 Enyart Road, Loveland, OH 45140 (US). THIEN, Joseph, Herbert [US/US]; 5998 Mackview Street, Fairfield, OH 45014 (US).		(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US). (81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: BLEACH-FREE AUTOMATIC DISHWASHING DETERGENT COMPOSITION HAVING ENZYME PARTICLES WITH ACID BARRIER COATING (57) Abstract A bleach-free liquid automatic dishwashing detergent composition is disclosed. The composition includes from about 0.1 % to about 10 % by weight of the composition of detergent enzyme composite particle including an enzyme containing core material, an acidic barrier layer coated on the enzyme containing core material, and a physical barrier layer coated on the acidic barrier layer. The composition also includes from about 0.1 % to about 99.9 % by weight of the composition of adjunct liquid automatic dishwashing detergent ingredients.		

THIS PAGE BLANK (USPTO)

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LJ	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

5

**BLEACH-FREE AUTOMATIC DISHWASHING DETERGENT COMPOSITION HAVING ENZYME PARTICLES WITH
ACID BARRIER COATING**

10

TECHNICAL FIELD

The present invention relates to liquid automatic dishwashing detergent compositions.
15 More particularly, the invention relates to a bleach-free liquid automatic dishwashing detergent product having enzyme composite particles which primarily have an acidic barrier coating and secondarily have a physical barrier coating for the protection of the enzyme composite particle.

BACKGROUND OF THE INVENTION

It is important to obtain enhanced cleaning performance against cooked on food soils from
20 a liquid automatic dishwashing detergent product (liquid ADW). The formulation of particulate ADWs with enzymes is well known in the art. However, in the context of liquid ADWs that are bleach-free, the incorporation of enzymes into the detergent composition still poses a challenge. One challenge is that the alkalinity of the liquid ADW attacks the enzyme and renders it ineffective over time. When the enzymes are incorporated into the liquid detergent by dispersing
25 the enzyme in a particulate material, it is necessary to somehow maintain the physical integrity of the particle containing the enzyme. That is not an easy task either, given the alkalinity of the liquid in which the enzyme particle must remain. Moreover, when formulating a liquid ADW composition with liquid enzymes, or with unprotected enzyme particles, it has been necessary to maintain product pH at a value equal to or less than about 9, as measured at 1% concentration, in
30 order to obtain enzyme stability in the liquid ADW composition during storage. It is well recognized that a higher pH is desirable for better cleaning performance.

In the past, enzyme particles have been coated with thick wax coatings in order to enable the formulation of higher alkalinity liquid ADWs, such as those with a pH value higher than about 9. However, wax coatings have one major disadvantage, i.e., they cause undesirable

filming on glass, stainless steel and plastic surfaces because of the water-insoluble waxes which melt and are released into the wash solution due to the high temperature encountered during the automatic dishwashing process. The filming problem is an even more problematic issue when no significant surfactants are present in the composition. Moreover, to achieve effective protection
5 of the enzyme against the alkalinity of the liquid ADW compositions, a high level of the wax coating has been needed, which further enhances the already undesirable situation of filming on dishes and glassware.

It has been desirable to have a liquid ADW product having enzyme containing solid particles that do not dissolve in the liquid product, but dissolve rapidly in the wash solution
10 during automatic dishwashing. It has been desirable to have a liquid ADW product having enzyme particles that do not cause a significant amount of unwanted filming on glass, stainless steel and plastic. It has been desirable to have a liquid ADW product having enzyme particles that are protected with a type of coating system that provides protection to the enzyme particle against the alkalinity of the liquid ADW product.

15 The inventors of the present invention have discovered that coating the enzyme composite particle with a chemical barrier coating, particularly an acidic barrier coating, effectively protects the enzyme particle from the alkalinity of the liquid ADW compositions. The inventors have also discovered that coating the enzyme composite particles already coated with an acidic barrier, with a physical barrier coating offers a complete protection to the enzyme particle. The physical
20 barrier protects the acidic barrier from reacting directly with the alkaline liquid product. The chemical barrier effectively neutralizes any stray hydroxyl groups of the alkaline product that permeate past the physical barrier coating. The physical barrier is thus also critical and the two coatings, i.e. physical and chemical barriers work together. The inventors of the present invention have discovered that coating the solid enzyme containing particles with polymeric
25 coatings which are insoluble in the liquid automatic dishwashing detergent composition but soluble in automatic dishwashing wash solution work as an effective physical barrier. Waxes are also effective as alternative physical barriers.

The present invention is thus directed to overcome one or more of the problems as set forth before.

30

BACKGROUND ART

U.S. Patent No. 5,164,106 discloses a non-aqueous liquid automatic dishwasher detergent composition containing a dual bleach system.

U.S. Patent No. 5,108,641 discloses an aqueous liquid automatic dishwasher detergent composition containing a dual bleach system.

U.S. Patent No. 4,965,012 discloses an encapsulating enzyme composition.

U.S. Patent No. 5,200,236 discloses a method for wax encapsulating particles.

5 U.S. Patent No. 3,908,045 discloses coating a solid bleach particle with a first layer of fatty acid and a second layer of base (alkali hydroxide) treated fatty acid.

SUMMARY OF THE INVENTION

The invention meets the needs above by providing a bleach-free liquid automatic
10 dishwashing detergent composition including from about 0.1% to about 10% by weight of the composition of deterative enzyme composite particle including an enzyme containing core material, an acidic barrier layer coated on the enzyme containing core material, a physical barrier layer coated on the acidic barrier layer, and from about 0.1% to about 99.9% by weight of the composition of adjunct liquid automatic dishwashing detergent ingredients.

15 DETAILED DESCRIPTION OF THE INVENTION

In the preferred embodiment of the present invention, the bleach-free liquid automatic dishwashing detergent composition includes from about 0.1% to about 10% by weight of the composition of deterative enzyme composite particle including an enzyme containing core material and an acidic barrier layer coated on the enzyme containing core material.

20 Acidic Barrier

In the preferred embodiment, the acidic barrier layer is formed from materials selected from the group consisting of organic acids, inorganic acids or polymeric acids. When the acidic barrier layer is formed from organic acids, the organic acids are selected from the group consisting of citric acid, maleic acid, malic acid, glutamic acid, succinic acid, and mixtures thereof. When the
25 acidic barrier layer is formed from inorganic acids, the inorganic acids are selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, and mixtures thereof and further, the inorganic acids absorbed in or adsorbed on polymeric coatings formed from materials selected from the group consisting of alkyl cellulose, polyvinyl alcohol, polyethylene glycol, alginate, polyvinylidene chloride, fluorocarbons and mixtures thereof. When the acidic barrier
30 layer is formed from polymeric acids, the polymeric acids are selected from the group consisting of non-neutralized or partially neutralized polyacrylic acid, modified polyacrylic acid, and mixtures thereof.

In the preferred embodiment, the acidic barrier layer is non-hygroscopic. The non-hygroscopicity is defined as thus: the acidic barrier layer is non-hygroscopic such that the acidic

barrier layer absorbs no greater than about 20% moisture by weight of the acidic barrier layer. the acidic barrier is exposed to 80% relative humidity for a period of about 1 week.

Physical Barrier

In the preferred embodiment, the bleach-free liquid automatic dishwashing detergent
5 product has enzyme particles having a combination of an acidic barrier coating and a physical
barrier coating for enhanced protection of the enzyme particle. The enzyme particle is first
coated with a chemical barrier coating and then with a physical barrier coating. This provides a
two-fold protection to the enzyme particle. The physical barrier coating effectively protects the
enzyme particle from the bulk alkalinity of the liquid ADW composition. The chemical barrier
10 effectively neutralizes any stray hydroxyls that permeate past the physical barrier coating, which
can be formed from polymers and waxes.

In one aspect of the present invention, physical barrier coating is formed from a
polymeric coating. The polymeric coating is prepared from materials selected from the group
consisting of alkyl cellulose ethers and polyvinyl alcohol. Other materials include paraffin
15 waxes, wax esters, paraffin wax and petrolatum mixture in a ratio in a range of from 30:1 to
about 10:1 by weight, paraffin wax and silicon mixture, paraffin wax, mica and silicon mixtures,
and paraffin wax, mica and petrolatum mixture. Alternative materials for the physical barrier
include fluocarbons and polyvinylidene chloride. Alternatively, the coating is prepared from
alginate. The particles remain undissolved or intact and unbroken in the liquid automatic
20 dishwashing detergent composition until the composition is used in an automatic dishwasher.
The liquid automatic dishwashing detergent product does not cause an increase in filming of
glassware or dishware as compared to a liquid automatic dishwashing detergent product not
having the above particles.

In the preferred embodiment, the acid barrier coated enzyme particles are further coated
25 with a polymeric coating which is insoluble in the liquid automatic dishwashing detergent
composition but soluble in automatic dishwashing wash solution. The polymeric coating is
prepared from materials selected from the group consisting of alkyl cellulose ethers. Desirably,
the alkyl cellulose ethers are either methyl cellulose or hydroxypropyl methyl cellulose (HPMC).
Preferably, the polymeric coating is prepared from methyl cellulose having a number average
30 molecular weight desirably in a range of from about 5000 to about 100,000, more preferably from
about 10,000 to about 20,000, and most preferably, about 14,000. The preferred methyl cellulose
is one sold under the trade name Methocel A15LV, and manufactured by Dow Chemicals.
Alternatively, the polymeric coating is polyvinyl alcohol (PVA) having a molecular weight,
desirably in a range of from about 5000 to about 100,000, and preferably from about 13,000 to

about 23,000. In one embodiment, the preferred PVA is from about 87% to about 89% hydrolyzed, such as a commercially available product having a trade name Airvol 205.

Process for forming polymeric coating on particles coated with acidic barrier

The process by which the polymeric coating is prepared and deposited upon the acid barrier coated enzyme particle is critical in order for the enzyme particles to remain undissolved in the liquid automatic dishwashing detergent composition and only become soluble in the wash solution during automatic dishwashing. It is desirable that the particles dispersed in the liquid ADW compositions do not break up or dissolve in the composition. It is also desirable that this be achieved without depositing an unduly thick coating of a polymeric material on the particle. It has been surprisingly discovered that when the polymeric material, such as methyl cellulose is sufficiently hydrated before spraying on the particle or prill, the polymer coated particle or prill remains stable, unbroken and undissolved in the liquid ADW composition. This hydration is achieved by forming a sprayable aqueous solution of the polymer (alkyl cellulose ether and/or polyvinyl alcohol) having a polymer concentration desirably in a range of from about 1% to about 30% by weight, preferably in a range of about 3% to about 20 %, more preferably in a range of about 3% to about 10 %, and most preferably, about 5%. Further, the temperature of aqueous solution of the polymer is desirably maintained within a range of from about 30 °C to about 40 °C while spraying the polymer solution on the particle, and preferably in a range of from about 32 °C to about 38 °C, and most preferably at a temperature of about 35 °C. It has been surprisingly found that by using a combination of the above process steps, i.e., the polymer solution being in a range of from about 1% to 30% by weight, and the spray temperature being in a range of from about 30 °C to about 40 °C, that a very stable, unbroken, continuous coating is formed on the particle or prill which is undissolved in the liquid ADW composition but soluble in the wash solution, while at the same time, requiring only about 5% polymer by weight of the particle. This offers an advantage because by using a smaller the quantity of polymer used for coating the enzyme particle, there is a reduction in the amount of polymer residue that can potentially re-deposit on the dishware and dishwasher, when the particle dissolves in the wash solution.

Preferably, the enzyme particles are colored. In one embodiment, the enzyme particles are colored and the automatic dishwashing liquid detergent composition is clear or translucent, so as to make the liquid automatic dishwashing product aesthetically pleasing. In another embodiment, the enzyme particles and the liquid automatic dishwashing detergent composition are both colored and the color of the particles is matched to the base color of the liquid composition. In one embodiment, the enzyme particles have a dark green color whereas the liquid composition has a light green color. Other preferred color combinations for the polymeric coating on the

enzyme particles and the liquid automatic dishwashing composition are: blue:blue, blue:white, green:green, green:white and green:yellow, respectively.

Desirably, the enzyme particles comprise from about 0.1% to about 5.0% by weight of the liquid composition, and preferably, from about 0.2% to about 1.0% by weight of the liquid composition.

The enzyme particles can be formed from various materials that do not cause any detrimental affect upon the performance of the liquid contains an enzyme, such as a prill. The core is coated with an acidic barrier coating and a polymeric coating as described before. The core can be made from sucrose, as an example. The method of forming prills is well known to those skilled in the art and is disclosed in the literature, such as for example, in U.S. Patent No. 4,965,012, which is incorporated herein by reference.

The enzyme particles can be of various sizes and shapes, such as spherical, oval, cylindrical or polygonal and desirably have a particle size in a range of from about 200 μm to about 5000 μm , preferably, from about 400 μm to about 2000 μm , and most preferably, from about 500 μm to about 850 μm .

Enzymes

The compositions of this invention may contain from 0 to about 8%, preferably from about 0.001% to about 5%, more preferably from about 0.003% to about 4%, most preferably from about 0.005% to about 3%, by weight, of active deterative enzyme. The knowledgeable formulator will appreciate that different enzymes should be selected depending on the pH range of the liquid ADW composition. Thus, Savinase® may be preferred in the instant compositions when formulated to deliver wash pH of 10, whereas Alcalase® may be preferred when the liquid ADWs deliver wash pH of, say, 8 to 9.

In general, the preferred deterative enzyme herein is selected from the group consisting of proteases, amylases, lipases and mixtures thereof. Most preferred are proteases or amylases or mixtures thereof.

The proteolytic enzyme can be of animal, vegetable or microorganism (preferred) origin. More preferred is serine proteolytic enzyme of bacterial origin. Purified or nonpurified forms of enzyme may be used. Proteolytic enzymes produced by chemically or genetically modified mutants are included by definition, as are close structural enzyme variants. Particularly preferred by way of proteolytic enzyme is bacterial serine proteolytic enzyme obtained from Bacillus, Bacillus subtilis and/or Bacillus licheniformis. Suitable commercial proteolytic enzymes include Alcalase®, Esperase®, Durazym®, Savinase®, Maxatase®, Maxacal®, and Maxapem® (protein engineered Maxacal); Purafect® and subtilisin BPN and BPN' are also commercially

available. Preferred proteolytic enzymes also encompass modified bacterial serine proteases, a variant of an alkaline serine protease from Bacillus, called Protease C, in which tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991, which is incorporated herein by reference. Genetically modified variants, particularly of Protease C, are also included herein. Some preferred proteolytic enzymes are selected from the group consisting of Savinase®, Esperase®, Maxacal®, Purafect®, BPN[®], Protease A and Protease B, and mixtures thereof. Bacterial serine protease enzymes obtained from Bacillus subtilis and/or Bacillus licheniformis are preferred. An especially preferred protease herein referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76 in combination with one or more amino acid residue position equivalent to those selected from the group consisting of +99, +101, +103, +107 and +123 in Bacillus amyloliquefaciens subtilisin.

Preferred lipase-containing compositions comprise from about 0.001 to about 0.01% lipase, from about 2% to about 5% amine oxide and from about 1% to about 3% low foaming nonionic surfactant.

Suitable lipases for use herein include those of bacterial, animal, and fungal origin, including those from chemically or genetically modified mutants. Suitable bacterial lipases include those produced by *Pseudomonas*, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034, incorporated herein by reference. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase produced from the microorganism *Pseudomonas fluorescens* IAM 1057. This lipase and a method for its purification have been described in Japanese Patent Application 53-20487, laid open on February 24, 1978, which is incorporated herein by reference. This lipase is available under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Such lipases should show a positive immunological cross reaction with the Amano-P antibody, using the standard and well-known immunodiffusion procedure according to Oucheterlon (Acta. Med. Scan., 133, pages 76-79 (1950)). These lipases, and a method for their immunological cross-reaction with Amano-P, are also described in U.S. Patent 4,707,291, Thom et al., issued November 17, 1987, incorporated herein by reference. Typical examples thereof are the Amano-P lipase, the lipase ex *Pseudomonas fragi* FERM P 1339 (available under the trade name Amano-B), lipase ex *Pseudomonas nitroreducens* var. *lipolyticum* FERM P 1338 (available under the

trade name Amano-CES), lipases ex *Chromobacter viscosum* var. *lipolyticum* NRR1b 3673, and further *Chromobacter viscosum* lipases, and lipases ex *Pseudomonas gladioli*. A preferred lipase is derived from *Pseudomonas pseudoalcaligenes*, which is described in Granted European Patent, EP-B-0218272. Other lipases of interest are Amano AKG and Bacillis Sp lipase (e.g. Solvay enzymes).

Suitable fungal lipases include those produced by *Humicola lanuginosa* and *Thermomyces lanuginosus*. Most preferred is lipase obtained by cloning the gene from *Humicola lanuginosa* and expressing the gene in *Aspergillus oryzae* as described in European Patent Application 0 258 068, incorporated herein by reference, commercially available under the trade name LipolaseR from Novo-Nordisk.

Any amylase suitable for use in a dishwashing detergent composition can be used in these compositions. Amylases include for example, 2-amylases obtained from a special strain of *B. licheniformis*, described in more detail in British Patent Specification No. 1,296,839. Amylolytic enzymes include, for example, Rapidase™, Maxamyl™, Termamyl™ and BAN™. In a preferred embodiment, from about 0.001% to about 5%, preferably 0.005% to about 3%, by weight of active amylase can be used. Preferably from about 0.005% to about 3% by weight of active protease can be used. Preferably the amylase is Maxamyl™ and/or Termamyl™ and the protease is Savinase® and/or protease B. As in the case of proteases, the formulator will use ordinary skill in selecting amylases or lipases which exhibit good activity within the pH range of the ADD composition.

Stability-Enhanced Amylase

Engineering of enzymes for improved stability, e.g., oxidative stability is known. See, for example J.Biological Chem., Vol. 260, No. 11, June 1985, pp 6518-6521.

"Reference amylase" hereinafter refers to an amylase outside the scope of the amylase
5 component of this invention and against which stability of an amylase within the invention can be measured.

The present invention also can make use of amylases having improved stability in detergents, especially improved oxidative stability. A convenient absolute stability reference-point against which amylases used in the instant invention represent a measurable improvement is
10 the stability of TERMAMYL (R) in commercial use in 1993 and available from Novo Nordisk A/S. This TERMAMYL (R) amylase is a "reference amylase". Amylases within the spirit and scope of the present invention share the characteristic of being "stability-enhanced" amylases, characterized, at a minimum, by a measurable improvement in one or more of: oxidative stability, e.g., to hydrogen peroxide/tetraacetylenediamine in buffered solution at pH 9-10; thermal
15 stability, e.g., at common wash temperatures such as about 60°C; or alkaline stability, e.g., at a pH from about 8 to about 11, all measured versus the above-identified reference-amylase. Preferred amylases herein can demonstrate further improvement versus more challenging reference amylases, the latter reference amylases being illustrated by any of the precursor amylases of which the amylases within the invention are variants. Such precursor amylases may
20 themselves be natural or be the product of genetic engineering. Stability can be measured using any of the art-disclosed technical tests. See references disclosed in WO 94/02597, itself and documents therein referred to being incorporated by reference.

In general, stability-enhanced amylases respecting the invention can be obtained from Novo Nordisk A/S, or from Genencor International.

25 Preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the Baccillus amylases, especially the Bacillus alpha-amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors.

As noted, "oxidative stability-enhanced" amylases are preferred for use herein. Such amylases are non-limitingly illustrated by the following:

30 (a) An amylase according to the hereinbefore incorporated WO/94/02597, Novo Nordisk A/S, published Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine (preferably threonine), of the methionine residue located in position 197 of the *B.licheniformis* alpha-amylase, known as TERMAMYL (R), or the homologous position

variation of a similar parent amylase, such as *B. amyloliquefaciens*, *B.subtilis*, or *B.stearothermophilus*;

(b) Stability-enhanced amylases as described by Genencor International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C.Mitchinson. Therein it was noted that bleaches in automatic dishwashing detergents inactivate alpha-amylases but that improved oxidative stability amylases have been made by Genencor from *B.licheniformis* NCIB8061. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8,15,197,256,304,366 and 438 leading to specific mutants, particularly important being M197L and M197T with the M197T variant being the most stable expressed variant. Stability was measured in CASCADE (R) and SUNLIGHT (R);

(c) Particularly preferred herein are amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S. These amylases do not yet have a tradename but are those referred to by the supplier as QL37+M197T.

Any other oxidative stability-enhanced amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple mutant parent forms of available amylases.

Enzyme Stabilizing System

For non-chlorine bleach containing formulations, the stabilizing system of the liquid ADWs herein may further comprise from 0% to about 10%, preferably from about 0.01% to about 6% by weight, of chlorine bleach scavengers, added to prevent chlorine species present in many water supplies from attacking and inactivating the enzymes, especially under alkaline conditions. While chlorine levels in water may be small, typically in the range from about 0.5 ppm to about 1.75 ppm, the available chlorine in the total volume of water that comes in contact with the enzyme during dishwashing is usually large; accordingly, enzyme stability in-use can be problematic.

Suitable chlorine scavenger anions are widely available, indeed ubiquitous, and are illustrated by salts containing ammonium cations or sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetracetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Other conventional scavengers such as bisulfate, nitrate, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, alcohol, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc. and mixtures thereof can be

used if desired. In general, since the chlorine scavenger function can be performed by several of the ingredients separately listed under better recognized functions, (e.g., other components of the invention including oxygen bleaches), there is no requirement to add a separate chlorine scavenger unless a compound performing that function to the desired extent is absent from an enzyme-containing embodiment of the invention; even then, the scavenger is added only for optimum results. Moreover, the formulator will exercise a chemist's normal skill in avoiding the use of any scavenger which is extremely incompatible with other optional ingredients, if used. For example, formulation chemists generally recognize that combinations of reducing agents such as thiosulfate with strong oxidizers such as percarbonate are not wisely made unless the reducing agent is protected from the oxidizing agent in the solid-form ADD composition. In relation to the use of ammonium salts, such salts can be simply admixed with the detergent composition but are prone to adsorb water and/or liberate ammonia during storage. Accordingly, such materials, if present, are desirably protected in a particle such as that described in U.S. Patent 4,652,392, Baginski et al.

15 Other ingredients

The liquid automatic dishwashing detergent composition optionally also contains from about 0.5% to about 20% of a dispersant polymer selected from the group consisting of polyacrylates and polyacrylate copolymers.

In the preferred embodiment, the liquid automatic dishwashing detergent product is highly viscous in a quiescent state and has a relatively high yield stress values. When subjected to shear stresses, however, such as being shaken in a container or squeezed through an orifice, the product quickly fluidizes and upon cessation of the applied shear stress, quickly reverts to a high viscosity state. The above liquid automatic dishwashing detergent product is preferably low foaming, readily soluble in the washing medium and most effective at pH values best conducive to improved cleaning performance, such as in a range of desirably from about pH 7.0 to about pH 13.0, and preferably from about pH 8.0 to about pH 12.0.

The physical stability of the liquid product may be improved and the thickness of the liquid product may be altered by the addition of a cross linking polyacrylate thickener to the liquid detergent product as a thixotropic thickener.

30 pH adjusting components

The pH adjusting components are desirably selected from sodium or potassium carbonate or sesquicarbonate, sodium or potassium silicate, citric acid, sodium or potassium bicarbonate, sodium or potassium borate, sodium or potassium hydroxide, and mixtures thereof. NaOH or KOH are the preferred ingredients for increasing the pH to within the above ranges. Other

preferred pH adjusting ingredients are sodium carbonate, potassium carbonate, and mixtures thereof.

Low Foaming Surfactant

The liquid nonionic surfactant detergents that can be used to practice the present invention are preferably are alkyl ethoxylates in non-chlorine bleach liquid ADW compositions. Alternatively, in chlorine bleach containing liquid ADW compositions, chlorine bleach stable low foaming surfactants are preferred and such surfactants are present in a range of from about 0.1% to about 10% by weight of the liquid composition. Such surfactants are generally known to one skilled in the art and need not be elaborated here, for purposes of brevity. One example of such a surfactant is an anionic surfactant commercially available under the trade name Dowfax.

To exemplify various embodiments of the present invention, Samples A, B, C, D, and E of the liquid automatic dishwashing detergent product compositions were formulated using the below named ingredients, as set forth in Example A.

		<u>EXAMPLE A</u>		
<u>Ingredient (weight % active)</u>		<u>A</u>	<u>B</u>	<u>C</u>
	Sodium Tripolyphosphate	17.5	16.0	---
	Potassium Tripolyphosphate	---	---	16.0
	Sodium Silicate	6.0	1.0	---
20	Potassium hydroxide	3.6	5.6	5.6
	Sodium hydroxide	2.0	2.0	2.0
	Polyacrylate polymer	1.0	---	---
	Nitric Acid	0.012	---	---
	Perfume	0.03	0.05	0.05
25	Nonionic surfactant	0.5	0.5	0.5
	Sodium Benzoate	---	---	---
	Sodium hypochlorite	---	---	---
	Polyacrylate polymer thickener	1.0	1.5	1.5
	Solid enzyme particles			
30	(4% active Protease)	0.5	0.5	0.5
	Solid enzyme particles			
	(4% active Amylase)	0.5	---	0.5
	Dye solution	---	---	0.001
	Propylene glycol	---	---	---

-13-

Boric Acid	---	---	---
Calcium chloride dihydrate	---	---	---
Water	Bal.	Bal.	Bal.
TOTAL	100.0	100.0	100.0

5

In the above compositions, the solid enzyme particles having a spherical shape, and a diameter of about 5 mm, are formed from a sucrose core coated with an acidic barrier coating formed from citric acid, and further coated with a polymeric coating as described above, and having a bluish-green color. The particles comprise about 0.1% to about 5% by weight of the liquid composition. The particles contain protease, amylase and a mixture of protease and amylase enzymes. The particles are insoluble in the liquid composition but are soluble or meltable in the wash solution during automatic dishwashing.

Accordingly, having thus described the invention in detail, it will be obvious to those skilled in the art that various changes may be made without departing from the scope of the invention and the invention is not to be considered limited to what is described in the specification.

15

WHAT IS CLAIMED IS:

1. A bleach-free liquid automatic dishwashing detergent composition, characterized by:
from 0.1% to 10% by weight of the composition of deterative enzyme composite particle including an enzyme containing core material;
an acidic barrier layer coated on said enzyme containing core material;
a physical barrier layer coated on said acidic barrier layer; and
from 0.1% to 99.9% by weight of the composition of adjunct liquid automatic dishwashing detergent ingredients.
2. A liquid composition according to claim 1, wherein said acidic barrier layer is formed from materials selected from the group consisting of organic acids, inorganic acids or polymeric acids.
3. A liquid composition according to claim 2, wherein said organic acids are selected from the group consisting of citric acid, maleic acid, malic acid, glutamic acid, succinic acid, and mixtures thereof.
4. A liquid composition according to claim 2, wherein said inorganic acids are selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, and mixtures thereof.
5. A liquid composition according to claim 2, wherein said polymeric acids are selected from the group consisting of non-neutralized or partially neutralized polyacrylic acid, modified polyacrylic acid, and mixtures thereof.
6. A liquid composition according to claim 1, wherein said acidic barrier layer is non-hygroscopic such that said acidic barrier layer absorbs no greater than 20% moisture by weight of said acidic barrier layer, when said acidic barrier is exposed to 80% relative humidity for a period of 1 week.
7. A liquid composition according to claim 2, wherein said acidic barrier layer is formed from inorganic acids absorbed in or adsorbed on polymeric coatings formed from materials selected from the group consisting of alkyl cellulose ethers, polyvinyl alcohol, polyethylene glycol, alginate, polyvinylidene chloride and mixtures thereof.

8. A liquid composition according to claim 1, wherein said physical barrier coating is formed from polymeric materials selected from the group consisting of alkyl cellulose ethers, polyvinyl alcohol and alginate.
9. A liquid composition according to claim 1, wherein said physical barrier coating is formed from methyl cellulose having a molecular weight in a range of from 5,000 to 100,000.
10. A liquid composition according to claim 1, wherein said physical barrier coating is formed from waxes, said waxes being selected from the group consisting of paraffin wax, bees wax, wax ester, paraffin wax and petrolatum mixture in a ratio in a range of from 30:1 to 10:1 by weight, paraffin wax and silicon mixture, paraffin wax, mica and silicon mixture, and paraffin wax, mica and petrolatum mixture.

INTERNATIONAL SEARCH REPORT

Internal I Application No
PCT/US 00/10388

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D3/386

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 277 532 A (NOVO INDUSTRI AS) 10 August 1988 (1988-08-10) claim 1 example 3 page 3, line 13 - line 19 page 4, line 21 - line 47	1,2,6
A	GB 1 309 431 A (UNILEVER LTD) 14 March 1973 (1973-03-14) claims examples page 2, line 74 - line 103	1-4,6-10
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

A document member of the same patent family

Date of the actual completion of the international search

4 August 2000

Date of mailing of the international search report

16/08/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Neys, P

INTERNATIONAL SEARCH REPORT

Internat Application No
PCT/US 00/10388

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 98 55577 A (PROCTER & GAMBLE) 10 December 1998 (1998-12-10) claims example figures 2,3 page 4, last paragraph -page 5, paragraph 1 page 19, paragraph 1 -page 20, paragraph 2	1,8-10
A	US 4 009 076 A (GREEN ROBIN JOHN ET AL) 22 February 1977 (1977-02-22) claims 1-8 examples 8-10,17,18 column 2, line 64 -column 3, line 18 column 3, line 57 - line 65	1-3,6
P,A	WO 99 32612 A (GENENCOR INT) 1 July 1999 (1999-07-01) claims 10-18 page 4, line 24 -page 7, line 5	1-3,6,8,9
A	GB 1 415 301 A (UNILEVER LTD) 26 November 1975 (1975-11-26) claims 1-14 examples page 2, line 32 - line 57 page 4, line 12 - line 38	1,2,5,6

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat. J. Application No

PCT/US 00/10388

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0277532 A	10-08-1988	AT 55779 T	15-09-1990
		AT 55778 T	15-09-1990
		DE 3764450 D	27-09-1990
		DE 3764460 D	27-09-1990
		DK 12188 A,B,	12-01-1988
		DK 61288 A	05-02-1988
		WO 8707292 A	03-12-1987
		EP 0270608 A	15-06-1988
		JP 63503390 T	08-12-1988
		US 4973417 A	27-11-1990
GB 1309431 A	14-03-1973	LU 58264 A	23-09-1970
		AT 296478 B	15-01-1972
		BE 747740 A	21-09-1970
		CH 527268 A	31-08-1972
		DE 2013300 A	08-10-1970
		DK 132038 B	13-10-1975
		DK 132038 A	
		ES 377739 A	01-11-1972
		FI 51491 B	30-09-1976
		FR 2039833 A	15-01-1971
		IE 33751 B	16-10-1974
		NL 131892 C	
		NL 7003964 A,B	23-09-1970
		NO 131892 B	12-05-1975
		PH 9554 A	16-01-1976
		SE 348220 B	28-08-1972
		ZA 7001853 A	24-11-1971
		ZM 3270 A	22-12-1971
WO 9855577 A	10-12-1998	EP 0988366 A	29-03-2000
US 4009076 A	22-02-1977	GB 1435905 A	19-05-1976
		AT 336529 B	10-05-1977
		AT 923273 A	15-09-1976
		BE 806856 A	30-04-1974
		CA 994266 A	03-08-1976
		CH 584234 A	31-01-1977
		DE 2354791 A	09-05-1974
		DK 139156 B	02-01-1979
		ES 420218 A	16-03-1976
		FR 2205532 A	31-05-1974
		IT 1004634 B	20-07-1976
		NL 7315113 A	07-05-1974
		SE 411769 B	04-02-1980
WO 9932612 A	01-07-1999	AU 2005299 A	12-07-1999
		EP 1021525 A	26-07-2000
GB 1415301 A	26-11-1975	FR 2160661 A	29-06-1973
		IT 975782 B	10-08-1974
		IT 975783 B	10-08-1974

THIS PAGE BLANK (USPTO)